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ABSTRACT

This note demonstrates the application of tert-butyldimethylsilylation to the determination of purity of an organophosphorus chemical warfare agent. This new technique allows detection and quantitation of alkylphosphonic acids down to picogram levels and has the advantages of being easy, quick, and relatively nonhazardous. Results from a gas chromatographic/mass spectrometric analysis of a VX sample using this derivatization technique are compared to those for the corresponding underivatized standard. The use of tert-butyldimethylsilylation as a routine technique for purity analysis of organophosphorus chemical warfare agents is recommended.

RÉSUMÉ

On décrit l'utilisation de la tert-butyldiméthylsilylation pour déterminer la pureté d'un agent chimique organophosphoré. Cette nouvelle technique, qui possède l'avantage d'être facile d'utilisation, rapide et relativement sans danger, permet de déceler et de doser les acides alkylphosphoniques en concentrations de l'ordre du picogramme. On compare les résultats des analyses par chromatographie en phase gazeuse d'échantillons de VX réalisées à l'aide de cette technique à ceux obtenus avec les étalons correspondants non transformés en dérivés. On recommande d'utiliser la tert-butyldiméthylsilylation comme technique courante pour vérifier la pureté des agents chimiques organophosphorés.

1.0 INTRODUCTION

The development of new CW agent detection methods, decontamination systems, protective equipment, and prophylactic and therapeutic materials requires that the purity of agents employed must be accurately determined for meaningful results to be obtained. A direct gas chromatographic analysis of a diluted VX sample will provide results only for VX and various volatile sulfide impurities. Phosphonic acids, which result from hydrolytic decomposition of VX, are of low volatility and accordingly will not elute from the gas chromatograph. With the recent development of a technique for the rapid and simple derivatization of alkylphosphonic and alkyl methylphosphonic acids [1], it is now possible to identify and quantify agent impurities that previously would have required more hazardous and labor-intensive procedures e.g. diazoalkylation [2]. This report describes the application of this technique, which involves forming the tert-butyldimethylsilyl (TBDMS) derivatives of free alkylphosphonic acids, to the analysis of stock VX solutions.

2.0 EXPERIMENTAL

2.1 Reagents and Derivatization Procedures

TBDMS-derivative standards were prepared as follows: Stock solutions of methylphosphonic acid (Fairfield Chemical Co., Blythewood, S.C., USA) and of ethyl methylphosphonic acid (kindly provided by Dr. E.W. Sarver, Chemical Research and Development Center, Edgewood, Maryland, USA) were made up in acetonitrile (silylation grade) to contain 5-7 µg/µL of acid. Silylation was then effected by diluting 10 µL of the acid stock solution with toluene (2.00mL), adding N-Methyl-N-(t-butyldimethylsilyl)trifluoroacetamide (200µL), (Regis Chemical Co., Morton Grove, Ill., USA) and heating at 60°C for one hour with constant stirring in a teflon-septum-sealed Reacti-vial (Pierce Chemical Co.). The cooled solution was injected directly into the GC or GC/MS for analysis.

Solutions of VX for analysis were made up in acetonitrile, diluted with toluene (2.00mL) to give concentrations of 100-135 ng/µL, and then similarly reacted with the silylation reagent. The VX used for this analysis originated from DREO pilot plant VX (lot no. RM1555-49; redistilled, Nov 1981; fraction #3) and had been stored in the freezer at -18°C. No stabilizers had been added.

2.2 Instrumentation

For the GC analyses, a Varian 3700 gas chromatograph equipped with an autosampler and a fused silica capillary column (DB5-30N, 0.25 µm coating,

30m x 0.322 mm, J&W Scientific Inc.), was used with the following operating parameters: FPD detector temperature, 250°C; injector temperature, 220°C; carrier gas, helium; flow-rate, 2.4 mL/min.; column temperature program, 60°C for 2 minutes followed by an increase to 250°C at 10°/minute and hold.

For the GC/MS analyses, a Finnigan 4530 gas chromatograph/quadrupole mass spectrometer was employed with a fused silica capillary column (DB5-30N, 0.25 μm coating, 23m x 0.258 mm I.D.) bracketed by an uncoated (65 cm x 0.255 mm) fused silica ion source inlet/transfer line deactivated with diphenyltetramethyldisilazane [3] (Chromatographic Specialties Ltd., Brockville) and a similarly deactivated fused silica capillary column injector retention gap (2 m x 0.32 mm). Column connections were made with Teflon/graphite/polyimide Butt connectors (Supelco Canada Ltd., Oakville, Ont.). Injections were effected using an on-column capillary injector (J&W Scientific Co.) with the injection end of the column withdrawn from the oven by approximately 10 cm and cooled by a flow of ambient air. The column was immediately retracted into the oven after injection. The GC temperature program employed was 110°C for 1 minute, increasing to 200°C at 10°/minute, then to 260 at 20°/minute and hold for 5 minutes. The mass spectrometer was operated under the electron impact mode with: electron multiplier, 1400V; emission current, 30 mA; electron energy, 70 eV; ion source, 80°C; manifold, 85°C; transfer line, 255°C; scanning 50 to 650 m/z at 0.5 sec/scan.

3.0 RESULTS AND DISCUSSION

Typical GC/MS analyses of an underivatized and the corresponding derivatized sample of VX are shown in Fig. 1. The top trace is the reconstructed ion chromatogram of a full scan analysis of a sample of VX before derivatization. Peak (E), the most abundant, was identified by its mass spectrum to be that of VX while the small peaks (F) and (G) were identified as sulfide impurities often observed in samples of VX. No other significant peaks were observed. The quantitative results of this analysis are given in Table 1 as the first set of relative area percentages and are based on the assumption that all components have identical ionization efficiencies. Without derivatization, analysis of this sample of VX (DREO Lot #RM1555-49, Fraction #3) would lead to the conclusion that the sample was 96% pure, the remaining 4% being the usual sulfide impurities.

The bottom trace in Fig. 1 is the reconstructed ion chromatogram of a sample of VX from the same batch but after TBDMS derivatization. Again, peaks (F) and (G) are the sulfide impurities observed in the underivatized sample. Peak (D) is also a sulfide impurity observed at low concentrations in some analyses of underivatized VX samples depending on the purity. Careful GC examination indicates that although it was observed in this derivatized sample

and not in the original material, TBDMS-derivatization does not appear to induce further decomposition of VX. The additional peaks (B) and (C) are always observed in any analysis involving this derivatization reagent. Peak (B) is seen in the TBDMS reagent itself and is believed to be 1,2-bis (t-butyldimethylsilyl)glycol. Likewise, characteristic ions in the mass spectrum of peak (C) indicate that it is a di-TBDMS compound as well [1]. Peak (A) was identified by electron impact to be the TBDMS derivative of ethyl methylphosphonic acid as determined previously [1] . The purity of the VX sample as determined by this analysis, based on a single point calibration and assuming again identical ionization efficiencies, is given in the final column of Table 1. Now the purity is seen more correctly to be 88% rather than the previously-determined 96% and the major impurity, ethyl methylphosphonic acid, is found to comprise 7 ± 3% (w/w) of the total components observed. No indication of any peak was observed at the retention time of the TBDMS derivative of methylphosphonic acid. Another VX sample from the same lot but from a later distillation fraction (fraction #4) was similarily derivatized and analyzed and was found to contain only a trace of the ethyl methylphosphonic acid derivative (0.5% w/w) and again, no indication of the TBDMS derivative of methylphosphonic acid.

Although the precision was higher using the autosampler-equipped GC, the quantitative data quoted herein originates from the GC/MS analysis because of the complete resolution of the ethyl methylphosphonic acid TBDMS derivative and one of the derivatized reagent impurities as compared to the corresponding analysis on the GC. This difference in resolving power on two essentially identical capillary columns is believed to be due to the different injectors installed on the respective instruments. The on-column injector system on the GC/MS coupled with a superior solvent effect brought about by the ambient temperature injection would be expected to provide a sharper more resolved chromatogram than the hot direct injector employed on the GC.

It was further determined during this investigation that care must be exercised in the specific order of sample analysis when testing for the presence of trace quantities of acidic decomposition products since these relatively involatile compounds can remain in the injector or the column. For instance, if an analysis of an underivatized impure sample of VX were followed by an injection of a derivatized mixture containing necessarily an excess of derivatizing reagent, a positive indication of the derivatized phosphonic acid residue from the previous injection would be readily detected. This problem was effectively eliminated by the injection of derivatizing reagent after a sample suspected of containing phosphonic acids had been analyzed.

It is evident from the reconstructed ion chromatograms that purity analysis of VX employing TBDMS derivatization is straightforward and simple.

Similar results are to be expected for other organophosphorus agents as well [1]. As the major degradation products of an organophosphorus agent are known to be the corresponding alkyl methylphosphonic acid and, ultimately, methylphosphonic acid [1], this derivatization procedure can provide an accurate indication of the purity of the sample by permitting simultaneous GC or GC/MS analysis for the agent and its major phosphorus-containing decomposition products.

TABLE 1

RESULTS FROM GC/MS ANALYSIS OF VX
LOT # RM1555-49 FR.3

Compound	Relative % by Area based on VX analysis*	Relative % by Area based on TBDMS/VX analysis
VX	96%	88%*
sulfides	4%	5%*
methylphosphonic acid	?	0%**
ethyl methylphosphonic acid	?	7%***

? = information unattainable without derivatization.
* = relative area percentages based on the assumption that sulfides and VX have similar ionization efficiencies.
** = less than 0.5 ng/μL based on a two-point calibration
*** = overall precision of ± 3% w/w of total sample based on a two-point calibration.

4.0 CONCLUSIONS

In this investigation, the general utility of TBDMS derivatization for purity analysis of VX, and indeed, of any phosphonic acid material, has been demonstrated. It is estimated that a complete analysis for phosphonic acids in VX could be performed within two to three hours including the necessary standards preparation and calibration. Based on studies on limits of detection (to be reported shortly [4]), it is estimated that levels of phosphonic acids down to 40 picograms per injection can be detected. In addition, the high stability of these derivatives allows the analysis of the sample to be carried out several weeks (if stored at room temperature), if

not months (at -18°C) after the derivatization has been effected. It is evident from this study that analysis for alkylphosphonic acids in VX by t-butyldimethylsilylation provides a straightforward, simple and rapid determination of the overall purity compared to other methods reported to date. Quantitative data on VX and its sulfur- and phosphorous-containing degradation products is provided. The excellent resolution and detectability recommend this procedure as an improved technique for the purity analysis of VX.

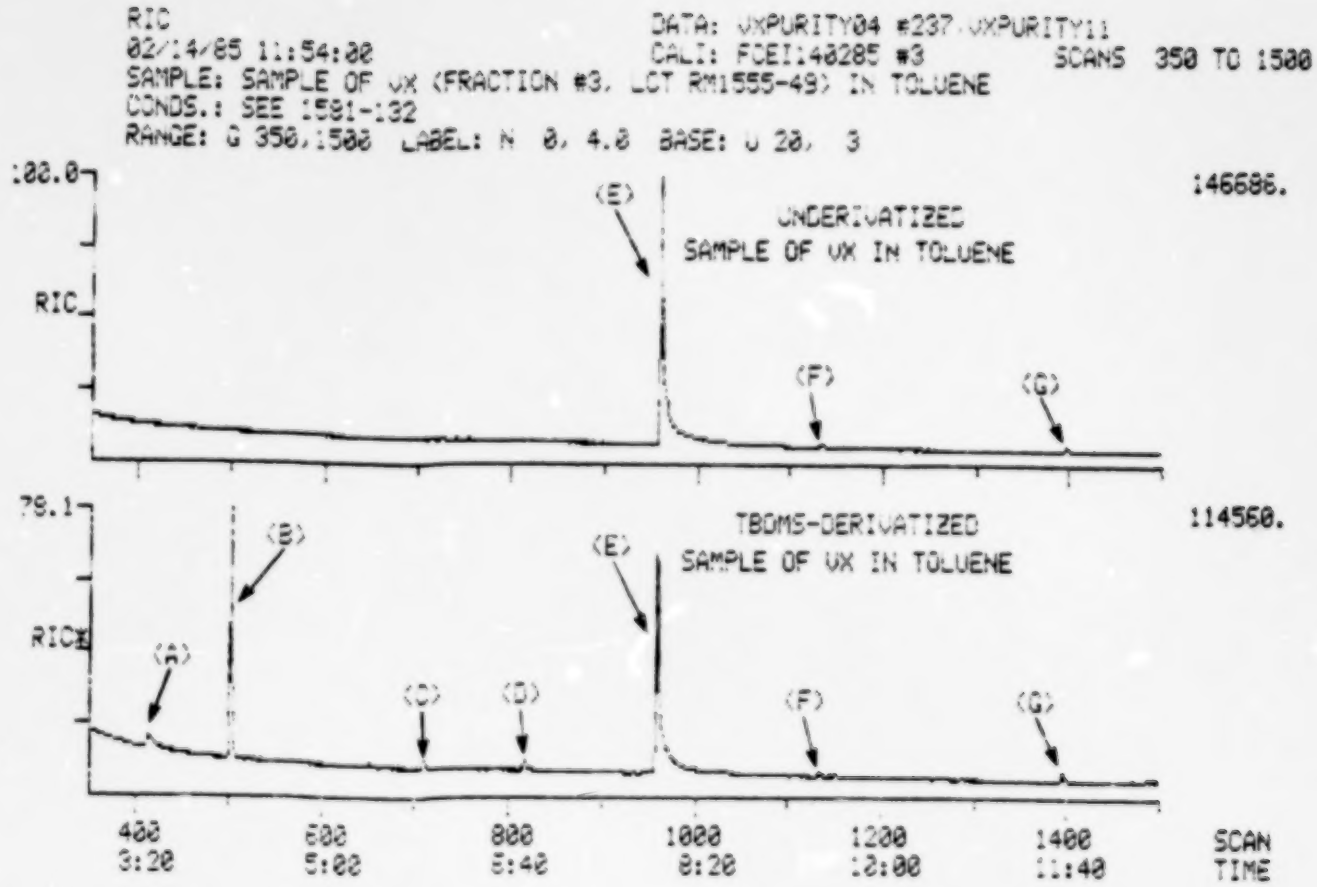

FIGURE 1. Comparison of analyses of solutions of VX and VX after TBDMS derivatization. Peaks (B) and (C) are TBDMS reagent impurities and are observed in blanks, (A) is TBDMS derivative of ethyl methylphosphonic acid, (E) is VX, (D), (F) and (G) are sulfides.

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